Renewable and Sustainable Energy Reviews 16 (2012) 1863–1873

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review on surface control of thermal radiation by paints and coatings for new energy applications

S. Wijewardane, D.Y. Goswami*

Clean Energy Research Center, University of South Florida, Tampa, FL 33620, United States

ARTICLE INFO

Article history:
Received 17 October 2011
Accepted 6 January 2012
Available online 18 February 2012

Keywords:
Electromagnetic radiation
Spectral selectivity
Surface emission
Selective paints

ABSTRACT

Emission of thermal radiation from a surface can be controlled spectrally and spatially, and the polarization and coherence of the radiation field can be modified. Of the various methods available for altering the radiation properties from a surface, paint and coatings possess a clear advantage regarding the cost, ease of application and simplicity. In this paper, we comprehensively review the capabilities of paint and coating technologies for emission control and for possible new energy-related applications. We also present an overview of the involved theories, common design and fabrication methods and possible future research opportunities to optimize these paints and coatings for spectral selectivity for specific applications.

Contents

1. Introduction

Control of thermal emission from surfaces to suit different requirements is very important in many applications, including energy conversion and micro–nano technologies. Radiation from a surface can be controlled spectrally and spatially, and the polarization and coherence of the radiation field can be modified. There are a number of methods, from commercially available paints to advanced surface gratings, which can modify the thermal emission from a surface. These methods have their own capabilities and limitations and can be used for a variety of applications. We have comprehensively reviewed these methods regarding the emission control capabilities and the range of possible applications. For each method an overview of the applicable theories and common design and fabrication methods are presented in this and a companion paper. In this paper, we focus on paints and coatings, which are different from other methods in a number of ways, such as, limitations of spectral control, involved technologies, economics and possible applications. In the following paper we will review more advanced types of thermal emission controlling mechanisms, such as, surface plasmon gratings and other photonic structures. Neither spatial directivity nor polarization can be controlled by paints or coatings alone. Paints and coatings are used to control the emission spectrally in a number of applications, however, only a limited spectral control is possible. All the past attempts to alter the surface radiation using paints and coatings are application-oriented. All the experimental procedures and the theoretical developments are targeted toward these well-established applications. Therefore

* Corresponding author.
E-mail address: goswami@usf.edu (D.Y. Goswami).

1364-0321/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.rser.2012.01.046

it is hard to find any general criteria such as those available for multilayer thin films and, 1D and 2D photonic structures, to develop a paint or coating for a new application.

The composition of the paper is as follows. First we summarize all the important past efforts to do spectral control of emission using paints and coatings separately, followed by a description of potential new applications of paint and coatings including some useful references for the material properties data, which are vital when designing a new paint or coating. Then we present a theoretical background related to spectrally selective paints and coatings followed by a discussion on the limitations and constraints of these selective layers to achieve their respective tasks. Next we set up a general method to form spectral selective paints and coatings for custom requirements. Finally we discuss present and possible future research opportunities to optimize these coatings for spectral selectivity for specific applications. This review covers only the aspects related to optics and spectral selectivity. For other aspects, such as, environmental issues, esthetic appearance and manufacturing, Refs. [1,2] provide an overview.

2. Paints and coatings: an overview

In the paint industry the term “paint” is used for its liquid phase and once it is applied to a surface it is called a “coating”. But in the field of spectral selective coatings, “paint” is generally considered as a type of coating; here we review “paint coatings” separately because of some attractive features such as ease of processing, low cost, ease of field maintenance, and commercial availability. Solar thermal conversion is the number one application of a spectrally selective paint or a coating, followed by radiative cooling. In solar thermal conversion, the aim is to maximize the solar absorption, i.e. maximize the absorptivity of wavelengths less than 3 μm and minimize the infrared emissivity of the wavelengths 3 μm or higher [3]. For the radiative cooling application, the complete opposite is desirable. With the oil-crisis in the early 1970s, research on techniques for optimizing solar energy usage got a kick-start including solar thermal conversion and radiative cooling. The research in these applications peaked in the early 1980s when a large number of research papers were published. Many good reviews [4,5] on paints and coatings for solar thermal applications were published in the early 1980s. A bibliography of the publications on selective paints from 1955 to 1981 can be found in [6]. Paints and coatings are also used in military applications such as camouflage techniques [7] and to change the infrared frequencies to interrupt radar detection [8]. Here the wavelength range of interest is 0.7–2.5 μm. In addition, these selective layers are used as a way of protecting the surfaces from high temperature sources, such as fire [9,10], where the requirement is to have high reflectance in the range of 1–9 μm.

2.1. Paints

Generally, paint is a dispersion of solid particles called “pigments” suspended in an organic medium called “resin.” Pigments are tiny insoluble particles included into the paint mainly to contribute color by absorption and reflection of light [11]. Resin is a macromolecular film forming agent that is either dissolved or dispersed in a solvent [12]. A majority of resins are organic silicones, which possess strong absorption bands in the middle infrared regions. Some common resins that are used are polyethylene [13], polyester [14], and propylene [15]. Paints can be applied by simple techniques such as roll coating also known as coil coating [16], dip coating [17], spin coating [18], and spray coating [19] or even by brush coating [20]. Thickness variations and surface roughness depend on these application techniques. Coil coating is the preferred coating process and it is described in many publications [21,22]. The solar absorptance and thermal emittance are higher in coil-coated layers than other common types, such as, sprayed layers due to the varying thickness and surface roughness.

Particle (pigment) size [23,24], volume concentration of pigments [25], the state of pigment dispersion [24], thickness of the paint layer [25–27] and paint application techniques influence the performance of spectral selective surfaces. Optimum particle size for a given optical property is a function of paint thickness and particle volume concentration [23]. Agglomeration and aggregation of large pigment particles make the dispersion process seldom perfect in actual paints, and thus change the anticipated optical properties [28].

Most of the pigments are complex metal oxide and semiconductors. Many types of pigments, carbon [29], FeO_x [30], melanin [31], Zn powder [32], silicon [28,33], PbS [34] organic soot (Degussa FW2) [35,36] are used in spectrally selective paints. TiO_2 (rutile titania) pigmented paints are the best for radiative cooling applications [37]. Opacity of these pigments is well discussed in [38]. Rutile titania pigments [39,40] hosted in polymer matrix are used in many selective paints for radiative cooling. $FeMnO_x$ is the best paint pigment so far for solar thermal applications [41]. The higher absorption of these pigments in the solar spectrum makes them suitable for thermal applications.

Basically two types of spectrally selective paints are discussed in the literature, based on the effect of paint thickness on the performance. They are “thickness sensitive spectrally selective” (TSSS) [42,43] and “thickness insensitive spectrally selective” (TISS) [44,45] paints. TSSS are the common types that currently dominate the market. These types of paints are incorporated with so-called “tandem structures”. The TSSS paint forms the top layer of these two-layer structures while an infrared reflective metal surface accounts for the bottom. Solariselect-Z^{TM} is a common commercially available TSSS paint for solar thermal applications with solar absorptance of 0.92 [46]. Various types of TISS paints are also well documented in the literature [47–49]. The infrared emissivity properties of the pigments are adequately used for these types of paints, as there is no reflective bottom surface.

2.1.1. Selective paints: present status

There are some intrinsic problems and limitations in achieving the ideal spectrally selective ranges, such as for solar thermal conversion. One is that in actual paint systems the dispersion process is not perfect. The state of dispersion depends upon the pigment particle size distribution and the particle size. The degree of pigment dispersion affects the optical and rheological properties of a paint system. Pigment particles appear in larger aggregates, agglomerates or flocculates of different sizes and shapes rather than in single discrete crystals. However there are newer technologies such as the supercritical fluid (SCF) technology [50,51] which present a new and interesting route for particle formation, avoiding most of the drawbacks of the traditional methods. Supercritical processes give micro- or even nanoparticles with narrow size distribution. Also the paint application techniques are not perfect. More advanced and more expensive paint application techniques could narrow the gap between the practical and ideal. There are a few commercially available thickness-sensitive spectral selective (TSSS) paints today. These paints can achieve solar absorptance of 0.94 and minimize the thermal emittance to 0.15 [52]. The question is whether the higher cost involved in the newer pigmentation technologies and advanced application techniques can be compensated by the output of these systems. The answer depends on many factors but in general, it tends to be more on the negative side. Considering the economical and esthetic aspects as well, it can be said that spectrally selective paints are nearly optimized. There is a great need to reduce or even completely eliminate the need for thickness control of paint coatings. This would give paint coatings wider versatility

for industrial and residential applications. The common method is to incorporate highly refractive metal particles in the paint system [53]. Previous research has been done on this subject, but none of them have resulted in successful thickness-sensitive paint.

2.2. Coatings

A variety of materials and composites can be exploited as spectrally selective coatings depending on the application. Oxide and sulfide layers were the first selective surfaces used in copper-based solar thermal systems [49]. Most metal films show high reflectance in the infrared region and semi-transparence in the visible region. Free electron metals such as Cu, Ag, Au show the best selective properties. These metals normally have very low emittance values around 0.02–0.04. Emissivity and reflectivity of most metals can be found in Refs. [54–56]. Also some inorganic compounds or metal/dielectric composites can be used as coatings for various applications. $Cr–Cr_2O_3$ known as black chrome [57] and Ni–Zn–S known as black nickel [58] are the inorganic materials used in the solar thermal industry. Thin coatings (less than 1 μm) of oxides, nitrides, oxinitrides and sulfides of Si can be used as selective infrared emitters [59]. Inorganic coatings of SiO [60], Si_3N_4 [61] and polymer coatings [62] are also suitable for high infrared emitting applications. Also semiconductors and doped semiconductors are intrinsically spectrally selective. They allow frequencies that are lower than their band gaps to pass, and absorb others. In the solar thermal industry semiconductor/metal tandems [63,64] are used for selective absorption in the solar spectrum. Cermets, which are formed by fine-grained mixtures of metallic and insulating components, can be used effectively for spectral emittance [65].

Selective coatings can be applied to a surface using a large number of techniques. Electroplating is one of the simplest coating techniques employed by the solar thermal industry for over 50 years. Chemical conversion [66], spray pyrolysis [67], vacuum deposition [68], and chemical vapor deposition [69] are the other common coating techniques.

3. Potential applications

One of the potential applications of the spectrally selective paints and coatings is to use high grade (high temperature) waste heat to produce electricity by means of infrared sensitive photovoltaic cells such as GaSb. This is a fairly new application of the thermophotovoltaic concept. The furnace exhaust temperatures in the glass, metal casting and steel industries are high enough for this application [70]. In fact this method can be used wherever fuel combustion occurs [71]. But the efficiency of the systems is low (1%) due to pragmatic problems, which hinder the optimal positioning of the photocell relative to the heat source. The shapes of these waste heat sources are quite arbitrary and the radiation intensities fluctuate both temporally and spatially. If the heat source and the system (photocell with selective emitter) are optimally positioned, then it is claimed to achieve efficiency of up to 70% [72]. One way to achieve this optimal positioning is by making the shape of the photovoltaic panels in harmony with the shape of the heat source [72]. But needless to say manufacturing of such random panel shapes would be expensive.

One cost effective method to increase the efficiency of these systems, might be to employ a spectrally selective paint on the interior of a fabricated enclosure which includes the heat source and photo cell. The fabricated enclosure could be any irregular shape depending on the space available. The paint could be designed to have either a high emissivity or reflectivity within the required spectral range depending on the on-site factors. A possible paint surface with high emissivity could absorb the energy from the heat source and emit the radiation toward the photocell, and a paint surface with a high reflectivity could reflect the radiation from the source toward the photocells.

In some applications, the spectrally selective paint with high emissivity may have to withstand temperatures as high as 1300 °C. At present high temperature paints are used in applications, such as, thermal protection of reusable space transportation systems during atmospheric reentry [73], and high temperature coatings are used in applications such as gas turbines and super heaters [74]. Rolls-Royce has developed paints for gas turbine engines that can withstand temperatures up to 1330 °C, and these paints are commercially available [75]. The main problem in developing a spectrally selective paint for high temperature applications is the selection of a pigment material. Carbon-based materials such as SiC are generally approved for these types of applications but these materials are prone to oxidation particularly at high temperatures. Although the oxidation can be prevented by applying an oxidation resistant coating it could well affect the spectral selectivity of the paint system. Also at these high temperatures chemical reactions could occur within the paint systems and such reactions could change the chemical composition leading to variations in the spectral as well as total emissivity [73]. So the paint or coating systems need to have chemical stability.

As described in the next sections it is not yet possible for paint coatings to emit as effectively in a narrow band spectrum as plasmon emitters and multilayer photonic emitters. However a reasonable selectivity could be gained to increase the efficiency of a thermophotovoltaic system considerably. The challenge is to make the paint less expensive so that it could be applied to a larger area enclosing the heat source and the photocell.

3.1. Absorption properties of selected materials

All most all the energy related applications of selective paints and coatings desire a high emittance at a particular frequency or within a particular frequency range. According to Kirchhoff's Law emissivity equals the absorptivity at a given frequency. Therefore we compiled the pigments (Table 1), resins (Table 2), and solvents (Table 3) with high absorption peak or high absorption frequency range that can be used to formulate paints with desired selective emittance. Also we tabulated selected paints (Table 4) and coatings (Table 5), which have high absorption at a particular frequency or within a frequency range.

4. Theoretical background

A good understanding of the appropriate theories for different applications is a prerequisite for designing and optimizing selective coatings. Theoretically, finding the reflectance of the coating in the interested frequency range is what is required by coating designers. In general, coatings are applied to surfaces in which transparency can be taken as zero. Therefore the absorptivity can be directly calculated, which according to the Kirchhoff's law is equal to the emissivity for a given frequency. Scattering of the radiation from the constituent particles is the most complicated phenomenon that occurs in a medium, which affects its optical properties. Therefore, if a medium has negligible scattering for a particular wave range, its optical properties can be calculated with ease. In a heterogeneous medium, where all the elemental particles are much smaller than the wavelength of interest, the scattering amplitude in the direction of an incoming beam can be neglected. At such a state the "effective medium theory" (EMT) can be used to calculate properties, such as, effective complex dielectric function of the composite medium from the known properties of the constituents. The Maxwell-Garnett theory and Bruggemann theory are the most

Table 1
Pigments with high absorption peak(s) or range. [56,76,77].

Pigments	Peak absorptance wave length(s) (μm)
Aluminum silicates	7.7
Calcium carbonate	6.7
Calcium phosphosilicate	9.5
Calcium borosilicate	9.8
Sodium silicates	10
Sodium sulfate	8.8
Calcite	7
Cobalt aluminate	15.4
Fe_2O_3	17.5, 25
Zinc chromate	2.9, 11.1
Asbestos	10.4
Cu, Cr (Black)	16.4, 19.2
Nichem	2.9, 6.2, 11.8
TiO_2	0.35
Pigments	**High absorptance wave length range (μm)**
Magnetite	2.5–4.45
Cu, Cr (Black)	0.5–2.5
Zn	2.5–10.5
$FeMnCuO_x$	1–0.2
Aluminum nitride	8–10
Beryllium oxide	7–8
Boron nitride	4–6, 9–20
Calcium silicate	5–12
Aluminum oxide	7–12
InSb	100–130
PbSe	30–50
Magnesium carbonate	7–13
$MoSi_2$	1–8
$3Al_2O_3{\cdot}2SiO_2$	5–15
NiO	8–15
MgO	8–15
SiO_2	5–15
Si_3N_4	4–15
ZnS	20–24
TaN	0.4–1
TeO_2	8–15
TiCl	20–50
ZrB_2	0.4–0.5
ZrN	0.4–0.6
ZrO_2	8–15
$ZrSiO_4$	6–15

commonly used effective medium theories [79]. These two theories are different regarding the considered type of microstructure. The Maxwell-Garnett approach deals with a separated grain structure (Fig. 1) in which particles of one material are dispersed in a continuous host of another material while the Bruggemann theory deals with an aggregate structure being a space filled with a random mixture of the two constituents (Fig. 2). In the Maxwell-Garnett approach, the effective dielectric function is given by

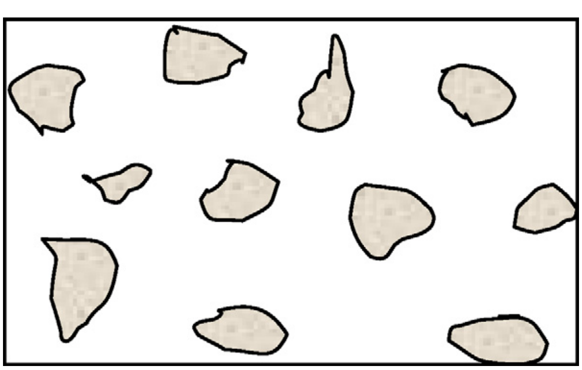


Fig. 1. Separated-grain structure.

Table 2
Resins with high absorption peak(s) [77].

Resin	Peak absorptance Wave length(s) (μm)
Poly(acrylamide)	6
Polyacrylic acid	5.8
Methyl methacrylate (acryloid)	5.8
Acrylic copolymer	5.8
Acrylate homopolymer	5.8
Poly(lauryl methacrylate)	3.4
Polymethacrylic	5.9
Alkyd	5.8
Cellulose acetate butyrate	5.7, 8.6
Cellulose acetate	5.7, 8.1
Methyl cellulose	9.3
Nitrocellulose	6, 7.8
Tetrafunctional epoxy resin	6.6
Epoxy novolac	6.6, 8.1
Polyglycol epoxy	9.1
Butyl glycidyl either epoxy	3.3, 8.9
Epoxy ester	3.4, 6.6
Amine based epoxy resin	6.6
Hydanation epoxy resin	5.8
Brominated bisphenol	3.4, 6.6, 8
Novolac epoxy	3.4, 6.8, 8.2, 9.8
Bisphenol	6.6, 8
Hexamethoxymethyl melamine	3.4, 6.4, 9.2
Methylated melamine formaldehyde	6.5
Methylol melamine	6.5
Metal salt of resin acids	3.4, 6.3
Polymerized resin	3.4, 5.8
Polyamide resin	3.4, 6
Isophthalate polyester	5.8, 8
Polyester polymers	5.8, 7.8
Polyethylene glycol	3.4, 8.9
Methyl vinyl ether	5.6
Polyvinyl ethers	3.3, 9.3
Polyglycol	2.9, 3.5, 8.9
polyethylenimines	3.4, 8.7
Polyurethane polymers	3.3, 4.5, 5.7, 8.2
Silicone	9.1
Dimethyl polysiloxane	7.9, 9.5, 12.5
Sodium methyl siliconate	8.9
Methyl phenyl polysiloxane	7.9, 9.5, 12.5
Polyvinyl butyral	3.4, 8.8, 10
Polyvinyl alcohol	3.4, 8.8, 10
Polystyrene	14.3
Polyvinyl acetate	5.7, 8.1
Polypropylene	3.4
Polyisobutylene	3.4
Vinyl acetate homopolymer	5.7, 8.1
Vinyl chloride homopolymer	3.4, 7, 7.9
Ammonium polyacrylate	5.8
Chlorinated polypropylene	13.7
Polyphenoxy phosphazene	6.7, 8.3, 10.5

$$\in MG = \frac{\in A + 2\in B + 2f(\in A - \in B)}{\in A + 2\in B - f(\in A - \in B)} \in B \qquad (1)$$

where $\in A$, $\in B$ are the dielectric functions of the host material and embedded particles, respectively. f is the filling factor. This theory has been widely used to interpret the experimental data on optical properties of various systems including metallic, dielectric and semiconducting particles. In the Bruggemann theory the effective dielectric constant $\in$Br is given by

$$f\frac{\in A - \in Br}{\in A + 2\in Br} + (1-f)\frac{\in B - \in Br}{\in B + 2\in Br} = 0 \qquad (2)$$

The derivation of these two theories can be found in [80] and [81], respectively. The validity and limitations of these two approaches are discussed in many publications. Maximum size limit is the major limitation of these theories. But a slight violation

Table 3
Solvents with high absorptance peak(s) [77].

Solvent	Peak absorptance Wave length(s) (μm)
Benzyl alcohol	3, 6.9, 9.1, 13.7
Butanol	3, 3.3, 7.4, 8.2, 10.9
Diacetone alcohol	5.9
Ethanol	3, 3.3, 9.5
Isobutanol	3, 3.3, 9.5
Methanol	3, 9.5
Ethyl acetate	5.7, 8
Ethyl isobutyrate	5.7, 8
Methyl amyl acetate	3.3, 5.7, 8
Cyclohexane	3.4
N-Pentane	3.4
Benzene	3.3, 6.8, 14.5
Carbon tetrachloride	12.8
Chloroform	8.2, 13.3
Perchloroethylene	11
Tetrachloroethane	8.3, 12.5, 13.3, 18.2
Trichlorobenzene	6.9, 9.2
Trichloroethane	9.3, 14.1
Dipentene	3.4, 6.9, 11.4
Turpentine	3.4
Tripolene	3.4
Acetone	5.8, 8.2
Pentoxone	3.3, 8.2, 7.4, 9.3
Propylene carbonate	5.6, 8.4, 9.5

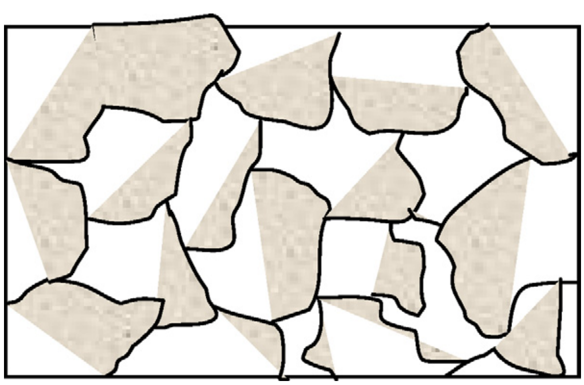


Fig. 2. Aggregate structure.

of the maximum size limits does not necessarily imply a collapse of the effective medium concept; extended theories [82–84] have been formulated to deal with such situations. Another assumption is that the inhomogeneous composite should possess macroscopic uniformity on a scale comparable with the wavelength range. Also it must be highlighted that these approaches are insufficient in frequencies close to the resonance frequencies of the dielectric constant of the small particles.

In heterogeneous structures where particle sizes are in the order of, or larger than the incident wavelengths, scattering plays a significant role and cannot be neglected. Multiple light scattering from such structures such as pigment particles dispersed in paint, paper, and polymer foils, can only be described precisely by radiative transfer theory or accurate Monte-Carlo simulations [85]. Rigorous solutions for the radiative transfer models often require numerical implementation. Finite volume method is the most used numerical technique for paint applications [86]. Approximate approaches are based on the concept of radiation exchange between different directions or "flux-channels" defined in the coating. "N flux model" is the most common radiative transfer model where the number of channels N can be selected depending on the required accuracy. Simple models with low number of channels are shown to be accurate for many numbers of applications. The Kubelka–Munk (KM) model which is almost universally used for multiple scattering applications, such as in paint films, represents a special case of N flux theories with $N = 2$. Because of the wide usage of this model in the paint and coating industry, as well as other industries such as paper, pigmented polymers, thermal insulations, dental composite resins and even in biological systems, and also for its simplicity and sufficient accuracy, a general description is presented below. In this model it is assumed that the radiation field inside the film consists of two isotropic diffuse fluxes, i.e. diffuse flux in the forward direction and reverse direction. The intensities of these fluxes can be coupled according to the radiative transfer differential equations. The KM theory provides a solution for this set of two equations to find out the diffuse reflectance from the film. It is given by

$$\text{Rkm} = \frac{1 - Rg[a - b \ \coth(bSh)]}{a + b \ \coth(bSh) - Rg} \tag{3}$$

where

$$a = \frac{S + K}{S} \tag{4}$$

$$b = \sqrt{a^2 - 1} \tag{5}$$

Rg – diffuse reflectance of backing substrate; h – film thickness.

The coefficient K determines the attenuation of diffuse fluxes resulting from absorption, and the coefficient S describes the net scattering of fluxes. More detailed derivation of this theory can be found in [87]. The derivation of the theory makes several assumptions for simplicity, hence has some limitations. The major assumption in this theory is that there are sufficient scattering particles in the film to diffuse the radiation completely, resulting in isotropic scattering. These types of "diffusion models" are good enough for applications in optically thick materials in which multiple scattering effects lead to isotropic distribution of the scattered radiation [88]; those assumptions limit the effective applicability to highly scattering and weakly absorbing coatings. Although the film is assumed to have plain parallel surfaces, in reality, surface

Table 4
Some selected paints with high absorptance peak(s) or range [78].

Paint	Peak absorptance wave length (μm)	Absorptivity
Antimony trioxide in potassium silicate binder	0.3	0.9
CaF_2 in sodium silicate binder (exposed to ultraviolet radiation)	0.3	0.8
Sodium aluminum silicate in sodium silicate binder (exposed to nuclear radiation)	0.4	0.9
TiO_2 in silicone resin binder	0.4	0.9
CeO_2 in barium beryllium silicate	9, 15	0.98

Paint	High absorptance wave length range (μm)	Absorptivity
Carbon (Lammblack) pigments in epoxy binder	0.2–40	0.9
Fe_3O_4 in silicone binder	6–20	0.9
ZnO in potassium silicate binder	0.2–0.4	0.95
Zinc sulfide in sodium silicate binder	0.2–0.3	0.9

Table 5
Some selected coatings with high absorptance peak(s) or range [78].

Coating	Peak absorptance wave length (μm)	Absorptivity
50% Co, 50% W on sandblasted substrate, heated to 1000 K	2	0.85
Al_2O_3 (0.4 mm thick) on roughened stainless steel substrate	9.5	0.98
$BaO{\cdot}TiO_2$ powder (0.127 mm thick) on Zr alloy substrate	11.5	0.98
B4C on inconel sandblasted substarte heated to 1000 K	5.10	0.99
Pyrolytic graphite, vapor deposited at 2400 K	1.5	0.83
TiO_2, (0.064 mm thick) on niobium substrate	0.7	0.95
Zirconium oxide on sandblasted inconel substrate	12	0.95
$ZrO_2{\cdot}SiO_2$ (0.1 mm thick) on Nb, Zr alloy substrate	8	0.95
Anodized Al (2 μm thick) sulfuric acid anodized	11	0.8
$NiCrO_x$ on stainless steel substrate	0.8	0.95
Si_3N_4 on Al substrate	10	0.95
Fe_2O_3 on stainless steel substrate	0.8	0.98
Cr_2O_3 on stainless steel substrate	0.8	0.85
CuO on stainless steel substrate	0.8	0.95
PbS on silver substrate	0.8	0.95

Coating	High absorptance wave length range (μm)	Absorptivity
Calcium titanate (0.09 mm thick) on rough niobium substrate	2–13	0.9
85% Cr_2O_3, 10% SiO_2 on mild steel substrate	2–14	0.9
Fe_2O_3 (0.03 mm thick)	3–21	0.9
Iron, titanium, aluminum oxide (0.1 mm thick) on Nb, Zr alloy substrate	1.5–13	0.9
$MgO{\cdot}Al_2O_3$, (0.13 mm thick) on Nb, Zr alloy substrate	6–12	0.9
KBr (7.5 μm thick) platinum substrate	104–108	0.98
Silicon carbide on aluminum oxide substrate (at 1000 K)	2–10	0.9
Strontium titanate (0.1 mm thick), on Nb, Zr alloy substrate at 1000 K	1.5–13	0.9
Armco blackened steel at 500 K	2–6	0.9
Oxidized stainless steel at 1200 K	2–15	0.9
Siliconized graphite	0.5–5	0.9
Silicon diffusion coating on molybdenum	2–10	0.9
Pack cementation (60% Al_2O_3, 40% Al) coating on niobium substrate	2–7.5	0.9
Co–Al_2O_3 on Al, Ni substrates	0.5–1	0.95
Oxidized surfaces		
Copper–aluminum alloy	0.3–0.7	
Iron	0.3–2.7	
Nickel	0.3–0.8	
Nickel–chromium–iron alloy	0.3–1.4	
Nickel molybdinum–iron alloy	0.3–2.4	
Titanium	0.2–0.7	

roughness is unavoidable. The KM coefficients K and S are empirically introduced in the theory and are usually determined from the measured diffuse reflectance by a curve fitting method. More recently, the Mie scattering [87] theory has been used to evaluate these coefficients with a reasonable accuracy. Using the Mie theory, the absorption and scattering parameters can be calculated from fundamental optical and morphological characteristics of particles. Various relations are suggested between calculated Mie coefficients and KM coefficients [89]. Application of KM or even rigorous radiative transfer theory requires correction for the surface reflection due to the refractive index change between the incoming wave media and the scattering media. For this reason KM models with corrections for surface reflections [90] are used. A more rigorous "four-flux" theory first introduced by Maheu et al. [91] considers four light traveling paths: diffuse up, diffuse down, directional up and directional down. These theories have been well-established in the selective paint industry since the late 1970s and were reported even 50 years ago. But today with the advancements in computer capabilities and simulation programs more rigorous calculations can be done in a short-time.

5. A brief criterion for selective paint formation

Spectrally controlling thermal emission has many advantages. Here a brief criterion is presented to design paint coatings for a given range of the spectrum. As the difficulties of producing narrow band selectivity are explained in another section here we consider only the relatively broader selectivity comparable for that required in solar thermal, and radiative cooling applications. Paint represents a complex multicomponent system. In most cases, the individual components, i.e. binder, solvent and pigment, are also of complex combination. The optical performance of a coating depends upon the properties of the substrate: paint layer thickness; complex refractive index of the matrix (resin); properties of scattering particles; complex refractive index; average size; volume fraction; degree of dispersion; and distribution across the layer [92]. Therefore the inverse calculation, i.e. finding the combination of pigments and pigment sizes for a given selective emission by calculation is almost impossible. However, there is a vast literature on spectral selectivity for many applications, such as camouflage coatings, fire protection coatings, and solar thermal applications, which represent a wide span of frequency range. Therefore it is possible to acquire much vital information such as pigment types and resin types to start designing paint with a custom selectivity. The most important factor is the composition of the constituents. Also it is essential to think about the method of application and the distribution of particles in the final dry coating, which strongly defines the final optical properties.

If paint is always applied on the same substrate then the optical properties of this substrate can be effectively used to obtain the required selectivity by combining the optical properties of the paint layer with those of the substrate. This is the method used in TSSS paints. On the other hand, if paint is to be applied on different types of surfaces then the paint layer must provide the required selectivity by itself and should avoid any "see through" effect of the substrate. These types of paints can be applied not only on any type of substrate but also on any arbitrarily shaped object, as there is no need for controlling the thickness as in the TSSS paints.

To determine the type of pigments and resins to start with, the following approximate procedure can be applied. For the frequency range in which high reflectivity is desired, the scattering coefficient of the paint should high. The scattering coefficient depends on the mutual effect of the optical properties of the constituents of paint film and it can be taken approximately as the ratio of the refractive indices of the pigment and the resin. The absorption of the paint layer largely depends on the intrinsic absorptivity of the pigment type. That means within the frequency range in which high reflectivity is desired, the imaginary (absorptive) part of the refractive index of the pigment should have a small value, and if high absorptivity or emissivity is preferred for some other frequency range, the pigment(s) should possess high absorption for that particular range. To achieve the selectivity between different spectral ranges it may be required to use a second pigment type as an extended pigment or filler but the incorporation of additional constituents always complicates the process and therefore should be avoided. Also pigments can be tailor-made to provide the required selective properties. One such pigment used in solar thermal applications is prepared by coating a thin layer of an appropriate black oxide to a highly reflecting metallic particle so that the combined pigment characterizes an absorber/reflector tandem as in TSSS paints. Although the absorption by the binder or resin could be neglected at the initial lay-out of the design most organic resins exhibit some absorption in the mid infrared range. A qualitative discussion on this issue can be found in [93].

Possible combinations of pigment types and resins can be found in the literature for the desired range of frequencies considering the above scenarios. The number of possible pigment types and resins can be further reduced by screening with respect to the environmental issues, durability, stability, and chalking effect.

Once possible types of pigments are identified, the size(s) of pigments can be calculated from the following approximate method. For a fixed value of scattering power "*m*" the wave length λ that is most efficiently scattered by a particle of diameter "*d*" is given by [94].

$$\frac{d}{k} = \lambda \tag{6}$$

In which

$$\frac{0.9(m^2+2)}{n\pi(m^2-1)} = k \tag{7}$$

where n is the refractive index of the resin.

Using these equations, the particle diameter d that could effectively scatter the mean of the desired frequency range can be calculated. It is important to note that this should be the diameter of the particles in the paint system, which might be different from the sizes of the commercially available particles due to the aggregates and agglomerates that are always present in the paint system. The sizes of these agglomerate particles can be reduced by paint dispersion techniques such as mechanical milling, but these processes are highly energy Intensive.

After gathering the required information such as resin types, pigment types and their sizes, a more rigorous calculation method can be used to optimize these parameters and to find other important parameters. With the advancement in the computer simulation, it is quite possible to model a detailed description of the potential paint layer with all the vital parameters. Optimizing the parameters by doing a complex and realistic calculation at this stage will reduce the number of costly repetitions at the testing stage, thereby reducing the overall cost involved in the paint development phase. Even though it is hard to include the effects of shapes and orientation of the agglomerate particles, there are some attempts [95] to find the light scattering properties of rutile particles with different characteristic morphological shapes using the finite-element method. Depending on the simulation results, parameters can be optimized using an iterative method. Changing the simulation parameters, such as, particle sizes and pigment-to-volume concentration (PVC) is vital and saves time. When PVC and thickness of the layer increases, the absorption coefficient and scattering coefficient values are normally expected to be higher because of the availability of more particles in which absorption and scattering can take place. When the mean particle size of the pigment accumulation increases, the longer radiation tends to scatter more effectively. Deviations from these scenarios are quite possible due to the high complexity of paint constituents.

After optimizing all the important parameters the paint should be formed and tested. The particle size is important for the optical properties and in general particle sizes in frequency-selective paints are larger than in normal commercial paints. In practice the dispersion will not be perfect and standard deviation of particle sizes could be different than anticipated. So there is no substitute for experiments and testing to find out the real picture. Determining the degree of dispersion in the dry paint film is vital for improvements. There are many techniques, such as, electron microscopy, light scattering method and flocculation gradient to find the degree of dispersion [96]. Based on the experimental results the parameters could be changed to obtain the desired selectivity as closely as possible. Optimization largely depends on how well the parameters can be controlled in the experiment.

6. Narrow spectral selectivity

As discussed in the previous sections most conventional applications require a wider spectral selectivity as compared to the newer applications, such as thermophotovoltaic which requires a sharp emissive peak at a particular frequency for maximum energy conversion. In conventional applications, such as solar thermal and radiative cooling, the spectral selectivity of paints and coatings has been achieved close to the ideal because of intensive research done over the last 50 years. However, achieving a narrow band spectral selectivity by paints or coatings is still a challenge. Achieving the required selectivity using paint or coatings would have a huge impact due to their cost effectiveness and ease of application, compared to other available technologies for narrow band selectivity. Here we discuss recent efforts to achieve narrow band selectivity, the current challenges and the possible directions of research that should be taken.

As discussed in the theoretical section, to change the spectral reflectance or emission and to obtain the required selectivity, the optical properties of the paints or coatings must be modified. The most important optical properties to achieve this task are absorption coefficient, scattering coefficient and in some cases, where interference is employed for selectivity, the refractive index. To use a narrower selectivity using the scattering effect, the paint or coating should have a scattering coefficient that has a peak or minima depending on the application with respect to the frequency in the vicinity of the targeted frequency. The scattering of visible and infrared radiation by a pigment is approximately a linear function of the difference between the refractive indices of the pigment and the resin. So, to have the required selectivity, the difference of refractive indices should have a maxima or minima with respect to the frequency. It is hard to find materials with such characteristics in nature, but there is a possibility to create such matter with the help of nanotechnology. A separate discussion on nano particles and nano technology is given in the next paragraph. For a fixed value of scattering power "*m*" the wave length λ that is most efficiently scattered by a particle of diameter "*d*" is given by Eq. (6).

The scattering power m of a pigment for white light is defined as the ratio between the refractive index of the pigment and the resin.

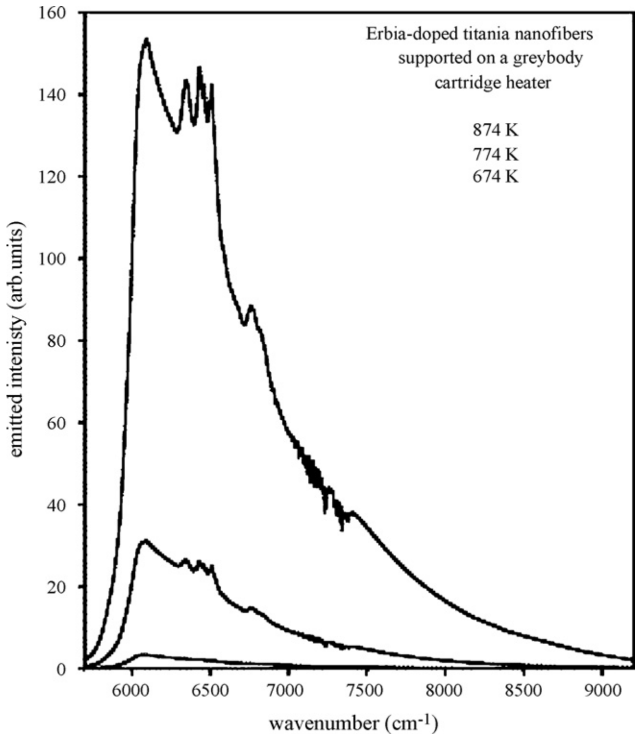


Fig. 3. Spectra of erbia doped titania nanofibers[98].

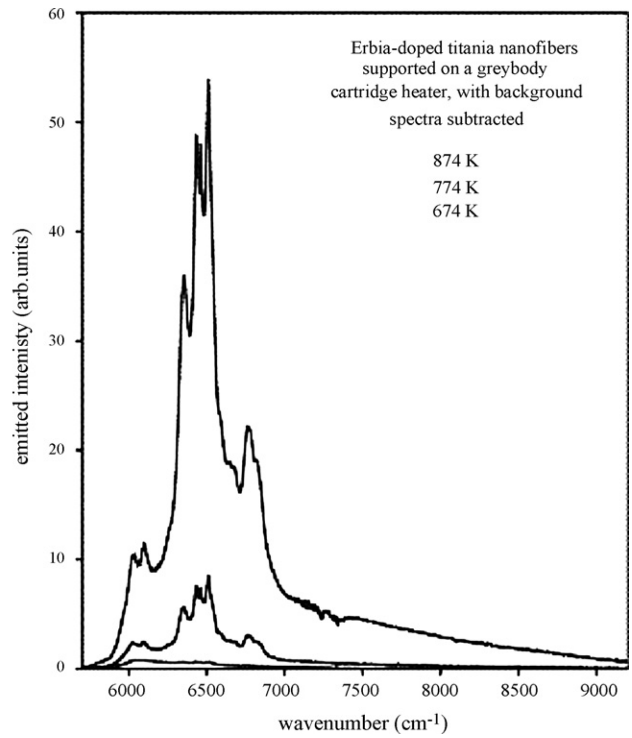


Fig. 4. Spectra of erbia doped titania nanofibers (background spectra substracted).

Here, as in Eq. (7), for a fixed refractive index n the relationship of the particle size and wave length is linear. This means that for a particular size, particles will scatter other wavelengths in the vicinity of the wave length of interest with almost the same efficiency as they would scatter the wavelength of interest itself. Also in practice it is not possible to regulate an exact particle size; a distribution of particle sizes with the mean equal to the required size is what one gets even from the best techniques. Therefore these distributions of particle sizes could effectively scatter the corresponding wavelengths according to Eq. (7), resulting in a dampened spectral peak. This is a disadvantage of paints and coatings where particles are an intrinsic constituent. The effect of the absorption coefficient on the selectivity is straight forward. A frequency-dependent absorption coefficient with the peak at a required frequency will result in a peak emissivity at that frequency. There are many materials that have absorption peaks at different wave lengths. Rare earth metals can be used as selective emitters in the infrared region due to their high absorption in this region [97]. Commonly, these metals are used as composites by mixing with other materials such as ceramic or titania because of the unavailability of these metals. The problem with these composites is that at higher temperatures grey-body like emission from other constituents' starts to dominate the rare earth metal's selective emission (Figs. 3 and 4). For applications, which require peaks of various wavelengths the absorption peaks have to be tuned or shifted and the answer again falls in the nano scale. The thin coatings that use the interference phenomena for spectral selectivity have their thickness controlled depending on the refractive index of the film and the surroundings to obtain the required spectral peaks. A rapid change of refractive index with the frequency in the vicinity of the interested frequency will enhance the selectivity. Here a peak of the refractive index at the interested frequency is not a necessity.

Nanosized metals and semiconductor particles show novel physical properties which are related to both classical and quantum size effects. Nano-composite materials consisting of metal or semiconductor particles embedded in various matrices have been of interest for a long time due to their tunable optical and physical properties. A large amount of research has been done on nanocomposite materials in which nanosized metal particles are embedded in insulators, while several investigations have also been carried out on metal particles embedded in a semiconductor matrix. At a low concentration of nano metal particles, the properties of the composites are almost similar to the properties of the host matrix, either insulator (ceramic) or semiconductor (Si), while by increasing the metal content the properties start to deviate more and more from the host materials. At a certain concentration of metal particles (known as the percolation limit) the composite properties start to show the properties of the bulk metal. This concentration range, where composite properties are changing from insulator/semiconductor properties to bulk metal properties, is known as the transition range. At this range, composites show some interesting optical properties such as peak absorptions at particular frequencies, and sudden step-up of the refractive index, which are not present in the bulk form of either material. These changes of optical properties, such as absorption resonance, can be qualitatively explained by resonant oscillations of surface charges in the electromagnetic field. The possibility of tuning the optical properties at this transition range to suit particular applications has attracted the interest of many researchers. As shown in the graph (Fig. 6) a peak of extinction coefficient at wavelength of 550 nm has appeared in the composite of Au and amorphous carbon [99]. The peak starts to further develop and shifts slightly toward the higher wavelengths with the increase of metal concentration up to the percolation limit. Also a step in the refractive index can be seen from 500 to 700 nm (Fig. 5). This sudden increment of refractive index can be utilized well to develop a thin coating with a sharp reflectance minimum in the vicinity of 600 nm, i.e. in between 500 and 700 nm. A nano composite made from Si–Ag with a co-sputtering technique shows a strong absorption peak at 610 nm with 40% Ag nano particles [100]. In contrast this absorption peak widens and weakens at a concentration level of 26% in a composite made from step sputtering [101]. Also another composite made by

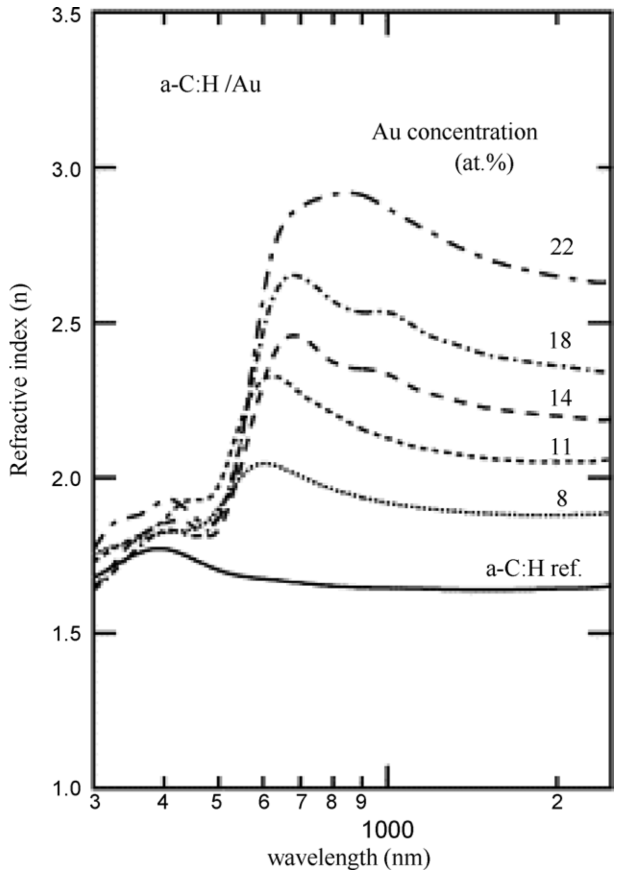


Fig. 5. Refractive index variations of composite of Au and amorphous carbon [99].

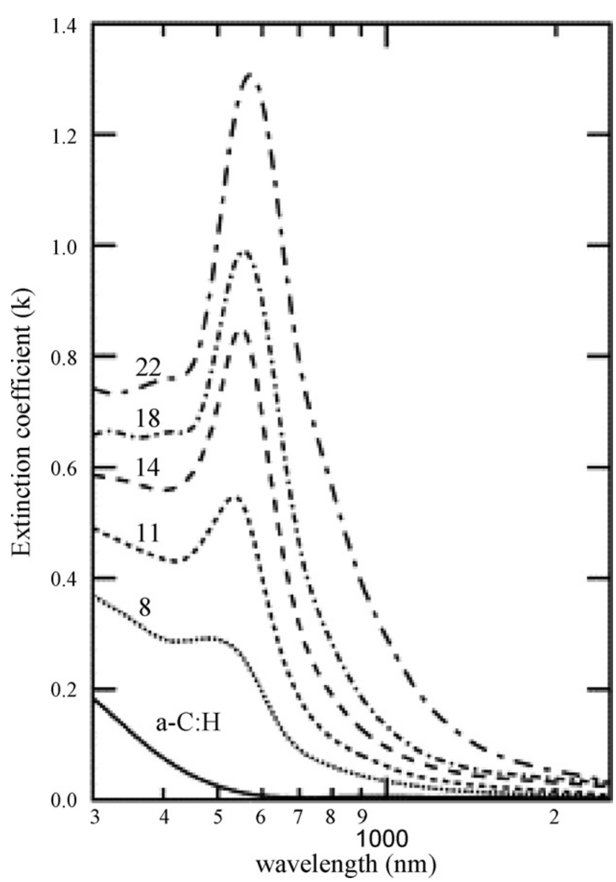


Fig. 6. Extinction coefficient variations of composite of Au and amorphous carbon.

embedding the Ag particles in an amorphous Si matrix shows two absorption peaks at 350 nm and 700 nm with Ag concentration of 40% [100]. These differences can be attributed to the different particle sizes and different nano structures developed with different forming techniques. Different nano structures limit the mean free path of the conduction electrons, and the particle sizes affect the band structure. These two effects modify the optical properties. The Sheng Ping effective medium theory [102], with the modification to account for the mean free path limitations, can be used to describe qualitatively the measured absorption spectra. These effective medium theories are not capable of describing the percolation phenomena, therefore they cannot be used to predict the outcome closer to the percolation threshold.

Even though there are number of researches conducted in these metal particles and insulator/semiconductor compounds, all of them have targeted the same type of materials and forming techniques, therefore, not much significant knowledge has been added for the last 4–5 years. Even if some nano coatings could produce the desired optical properties, their applicability as a usable coating in practice is subject to many other important properties. These coatings should have good adhesion for some suitable substrates, thermal stability and durability for the desired application.

7. Conclusion

With the increased significance of clean energy, researches are expanding their horizons to explore newer techniques that could produce electricity cleanly and effectively. The nano-scale antenna technique and conversion of the high-grade waste heat-to-electricity by thermophotovoltaics are such methods that require a significant modification of the radiation emitting from the source for a higher efficiency. From the various methods for altering the radiation properties from a surface, paints and coatings possess a clear advantage regarding the cost, ease of application and simplicity. However, some vital improvements need to be made for these innovations to obtain the required performances comparable to existing conventional energy conversion techniques. With the perception of this requirement this review has presented vital information that would be highly beneficial in achieving the required level of performance. This paper comprehensively elaborates the involved theoretical background, presents a general criterion for paint forming and describes the challenges and possible methods for achieving the requisite tasks.

References

[1] Bentley J, Turner GPA. Introduction to paint chemistry and principles of paint technology. Chapman and Hall; 1998.
[2] Paul S. Surface coatings: science & technology. 2nd edition J. Wiley; 1996.
[3] Meinel AB, Meinel MP. Applied solar energy: An introduction; 1976, chapter 9.
[4] Bogaerts WF, Lampert CM. Review – materials for photothermal solar energy conversion. Journal of Material Science 1983;18:2847–75.
[5] Agnihotri OP, Gupta BK. Solar selective surfaces. New York: Wiley; 1981.
[6] Niklasson GA, Granqvist CG. Surfaces for selective absorption of solar energy – an annotated bibliography 1955–1981. Journal of Material Science 1983;18:3475.
[7] Pipoly R. Polymer Paint Colour Journal 1989;179:357.
[8] Supcoe RF. Coatings for infrared camouflage, Rep. C-3946. Annapolis, MD: David Taylor Research Center; 1974.
[9] Berdahl P. Pigments to reflect the infrared radiation from fire. Journal of Heat Transfer 1995;117:355–8.
[10] Ellis H, Fire barrier coating and fire barrier plywood. US patent No. 5,130,184, 1992.
[11] Klanj M, Gundea S, Orela ZC. The influence of paint dispersion parameters on the spectral selectivity of black-pigmented coatings. Solar Energy Materials & Solar Cells 2003;80:239–45.
[12] Bullet TR. Paint a surface modifier. Physics in Technology 1983;14:119–25.
[13] Akhtarkhavari A, Kortschot MT, Spelt JK. Adhesion and durability of latex paint on wood fiber reinforced polyethylene. Progress in Organic Coatings 2004;49:33–41.

[14] McFadden J, Scheuing DR. Determination of polyols in silicone-polyester resins and paint films. Journal of Chromatographic Science 1984;22:310–2.
[15] Tomasetti E, Legras R, Henri-Mazeaud B, Nysten B. Plastic deformation in polypropylene/(ethylene–propylene) copolymer blend during paint debonding. Polymer 2000;41:6597–602.
[16] Orel B, et al. Coil-coating paints for solar collector Panels-I. Solar & Wind Technology 1990;7:609–705.
[17] Cui Z, Yin L, Wang Q, Ding J, Chen Q. A facile dip-coating process for preparing highly durable super hydrophobic surface with multi-scale structures on paint films. Journal of Colloid and Interface Science 2009;337:531–7.
[18] Conceicao TF, Scharnagl N, Blawert C, Dietzel W, Kainer KU. Corrosion protection of magnesium alloy AZ31 sheets by spin coating process with poly(ether imide) [PEI]. Corrosion Science 2010;52:2066–79.
[19] Whitehouse NR. Paint application, Shreir's corrosion; 2010 [chapter 4.10], p. 2637–42.
[20] Bierwagen GP. Film coating technologies and adhesion. Electrochimica Acta 1992;37:1471–8.
[21] Orel ZC, Orel B. Thermal stability and cross-linking studies of diisocyanate cured solar absorptance low-emittance paint coatings prepared via coil-coating process. Solar Energy Materials and Solar Cells 1995;36:11–27.
[22] Santos D, Costa MR, Santos MT. Performance of polyester and modified polyester coil coatings exposed in different environments with high UV radiation. Progress in Organic Coatings 2007;58:296–302.
[23] Erik S, et al. Light-scattering properties of titania particles studied using a finite-element method. Journal of American Ceramic Society 1998;81:469–79.
[24] Perera YD. Effect of pigmentation on organic coating characteristics. Progress in Organic Coatings 2004;50:247–62.
[25] Gunde MK, et al. Optimum thickness determination to maximize the spectral selectivity of black pigment coatings for solar collectors. Thin Solid Films 1996;277:185–91.
[26] Williams DA, Lappin TA, Duffie JA. Selective radiation properties of particulate coatings. Journal of Engineering for Power-Transactions of the ASME 1963;85:213.
[27] Malhotra LK, et al. Partly selective Black paint coatings. Energy Research 1981;5:393–6.
[28] Orel ZC, et al. Spectrally selective silicon paint coatings. Solar Energy Materials & Solar Cells 1996;40:197–204.
[29] Schmitt CR, Schreyer JM, et al. Solar selective carbon coatings. Carbon 1977;15:432.
[30] Agarwal RC, Pillai PKC. Selective blacks for enhanced photothermal solar energy conversion. Energy Conversion and Management 1981;21:239–51.
[31] Gallas M, Eisner M. Melanin pigmented solar absorbing surfaces. Proceedings of the American section of the international solar energy society. Phoenix 1980;3:1118.
[32] Orel ZC, Orel B. Preparation and characterization of low emitting black Zn pigment for spectrally selective paints. Solar Energy Materials 1991;21:267–81.
[33] Smith GB, Gentle A, Swift PD, Earp A, Mronga N. Colored paints based on iron oxide and silicon oxide coated flakes of aluminum as the pigment, for energy efficient paint: optical and thermal experiments. Solar Energy Materials and Solar Cells 2003;79:179–97.
[34] Agarwal RC, Pillai PKC. Chemically sprayed PbS coatings for photothermal solar energy conversion. Applied Energy 1982;11:61–8.
[35] Orel B, et al. Organic Soot pigmented paints for solar panels. Solar & Wind Technology 1986;3:45–52.
[36] Tesfamichael T, Hoel A, Ckelga EW, Gunnar R. Optical characterization and modeling of black pigments used in thickness-sensitive solar-selective absorbing paints. Solar Energy 2000;69(Suppl.):35–43.
[37] Harrison AW, Walton MR. Paint. Solar Energy 1978;20:185–8.
[38] Balfour J. Opacity and titanium dioxide pigments. Pigments 1990;6:225–30.
[39] Orel B, Gunde MK, Krainer A. Radiative cooling efficiency of white pigmented paints. Solar Energy 1993;50:477–82.
[40] Vargas WE, Greenwood P, Otterstedt JE, Niklasson GA. Light scattering in pigmented coatings: experiments and theory. Solar Energy 2000;68:553–61.
[41] Smith GB, Granqvist CS. Green, nanotechnology: solutions for sustainability and energy in the built environment. CRC Press; 2010.
[42] Etherden N, Tesfamichael1 T, Niklasson GA, Wäckelgård E. A theoretical feasibility study of pigments for thickness-sensitive spectrally selective paints. Journal of Physics D: Applied Physics 2004;37:1115–22.
[43] Lundh M, Blom T, Wäckelgård E. Antireflection treatment of thickness sensitive spectrally selective (TSSS) paints for thermal solar absorbers. Solar Energy 2010;84:124–9.
[44] Orel B, Spreizer H, Vuk AS, Fir M, Merlini D, Vodlan M, Kohl M. Selective paint coatings for colored solar absorbers: polyurethane thickness insensitive spectrally selective (TISS) paints (part II). Solar Energy Materials & Solar Cells 2007;91:108–19.
[45] Orel B, Spreizer H, Slemenik Perše L, Fir M, Šurca Vuk A, Merlini D. Silicone-based thickness insensitive spectrally selective (TISS) paints as selective paint coatings for colored solar absorbers (part I). Solar Energy Materials & Solar Cells 2007;91:93–107.
[46] Orel B, et al. Coil-coating paints for solar collector panels-II. Solar & Wind Technology 1990;7:713–7.
[47] Kunič R, Koželj M, Orel B, Šurca Vuk A, Vilčnik A, Slemenik Perše L, Merlini D, Brunold S. Adhesion and thermal stability of thickness insensitive spectrally selective (TISS) polyurethane-based paint coatings on copper substrates. Solar Energy Materials and Solar Cells 2009;93:630–40.
[48] Wilson D. Spectrally selective surfaces for copper based solar thermal energy converters: surface finishes on copper and copper alloys. In: CDA Seminar. 1983.
[49] Hutchins MG. Spectrally selective solar absorber coatings. Applied Energy 1979;5:251–62.
[50] Hakuta Y, Hayashi H, Arai K. Fine particle formation using supercritical fluids. Current Opinion in Solid State and Materials Science 2003;7:341–51.
[51] Yeo S, Kiran E. Formation of polymer particles with supercritical fluids: a review. The Journal of Supercritical Fluids 2005;34:287–308.
[52] Tesfamichael T, Hoel A, Wäckelgård E, Niklasson GA, Gunde MK, Orel ZC. Optical characterization and modeling of black pigments used in thickness-sensitive solar-selective absorbing paints. Solar Energy 2001;69:35–43.
[53] Japelj B, Vuk A, Orel B, Perše L, Jerman I, Kovač J. Preparation of a TiMEMO nanocomposite by the sol–gel method and its application in colored thickness insensitive spectrally selective (TISS) coatings. Solar Energy Materials and Solar Cells 2008;92:1149–61.
[54] Palik ED. Handbook of optical constants of solids I. Academic Press; 1985.
[55] Palik ED. Handbook of optical constants of solids II. Academic Press; 1991.
[56] Aleksander S. Radiant properties of materials: tables of radiant values for black body and real materials. New York: Elsevier; 1986.
[57] McDonald GE. Spectral reflectance properties of black chrome for use as a solar selective coating. Solar Energy 1975;17:119–22.
[58] John S, Shanmugam NV, Srinivasan KN, Selvam M, Shenoi BA. Blackening of electrolysis nickel deposits for solar energy applications. Surface Technology 1983;20:331–8.
[59] Karlsson B, et al. Optical properties of some metal oxides in solar absorbers. Physica Scripta 1982;25:826–31.
[60] Granqvist CG. Spectrally selective coatings for energy efficiency and solar applications. Physica Scripta 1985;32:401–7.
[61] Randich E. Thin Solid Films 1981;83:393.
[62] Rabek JF. Applications of polymers in solar energy utilization: review article. Progress in Polymer Science 1988;13:83–188.
[63] Warren RW. Solar selective surfaces made of semiconductor powders. In: Proceedings of the ASME winter annual meeting. 1974. p. 75.
[64] Martin PJ. Thin Solid Films 1982;87:203.
[65] Granqvist CG. Optical properties of cermets materials. Journal de Physique 1981;42:247.
[66] Papini M. Chemical, structural and optical characterization of Ni···P chemical conversion coatings for photothermal absorption of solar energy. Solar Energy Materials 1986;13:233–65.
[67] Chidambaram K, Malhotra LK, Chopra KL. Spray-pyrolysis cobalt black as a high temperature selective absorber. Thin Solid Films 1982;87:365–71.
[68] Peterson MJ, Cocks FH. Selenium and tellurium selective absorber coatings produced by an oblique vacuum deposition technique. Solar Energy 1980;24:249–53.
[69] Halary-Wagner E, Bret T, Hoffmann P. Light-induced chemical vapor deposition painting with titanium dioxide. Applied Surface Science 2003;208: 663–8.
[70] Thermophotovoltaic electric power generation using exhaust heat: EEE Blog; February 11, 2007.
[71] Butcher TA, Hammonds JS, Horne E, Kamath B, Carpenter J, Woods DR. Heat transfer and thermophotovoltaic power generation in oil-fired heating systems. Applied Energy 2011;88:1543–8.
[72] Hegner M, Generating PV. Electricity without solar radiation? Refocus 2005;6:13.
[73] Neuer G, Jaroma-Weiland G. Spectral and total emissivity of high-temperature materials. International Journal of Thermophysics 1998;19:917–29.
[74] Bird C, Mutton JE, Shepherd R, Smith MDW, Watson HML. Surface temperature measurement in turbines. In: AGARD conference proceedings. 1998. p. 598–621.
[75] Brandt R, Bird C, Neuer G. Emissivity reference paints for high temperature applications. Measurement 2008;41:731–6.
[76] Lewis P. Pigment handbook. 2nd ed. John Willey & Sons; 1988.
[77] An infrared spectroscopy atlas for the coatings industry. Federation of Societies for Coatings Technology 1980.
[78] Touloukian YS. Thermal radiative properties: coatings. New York: IFI; 1972.
[79] Niklasson GA. Effective medium models for the optical properties of inhomogeneous materials. Applied Optics 1981;20:26.
[80] Kerker M. The scattering of light and other electromagnetic radiation. New York: Academic; 1969.
[81] van de Hulst HC. Light scattering by small particles. New York: Wiley; 1957.
[82] Weissker H, et al. Validity of effective-medium theory for optical properties. Physical Review B 2003;67:165322.
[83] Sancho-Parramon1 J, Janicki V. Effective medium theories for composite optical materials in spectral ranges of weak absorption: the case of Nb_2O_5–SiO_2 mixtures. Journal of Physics D: Applied Physics 2008;41:295–304.
[84] Joerger R, et al. Optical properties of inhomogeneous media. Solar Energy Materials and Solar Cells 1998;54:351–61.
[85] Freireich B, Wassgren C. Intra-particle coating variability: analysis and Monte-Carlo simulations. Chemical Engineering Science 2010;65:1117–24.
[86] Thiele ES, French RH. Computation of light scattering by anisotropic spheres of rutile titania. Advanced Materials 1998;10:1271–6.
[87] Bhavsar MC, et al. Estimation of Kubelka–Munk coefficients and comparisons with theoretically predicted values using Mie theory parameters. Paint & Resins June 1986.

[88] Vargas WE, Niklasson GA. Applicability conditions of the Kubelka–Munk theory. Applied Optics 1997;36:5580.
[89] Gunde MK. Absorption and scattering of light by pigments particles in solar-absorbing paints. Applied Optics 2000;39:622–8.
[90] Orel ZC, et al. Application of Kubalka-Monk theory for the determination of the optical properties of solar absorbing paints. Progress in Organic Coatings 1997;30:59–66.
[91] Maheu B, Letoulouzan JN, Guesebet G. Four-flux models to solve the scattering transfer equation in terms of Lorenz–Mie parameters. Applied Optics 1984;23:3353–62.
[92] Orel ZC, Gunde MK. Spectrally selective paint coatings: preparation and characterization. Solar Energy Materials and Solar Cells 2001;68:337–53.
[93] Chalmers JM. Infrared spectroscopy in the analysis, characterization, and testing of coatings. JCT Journal of Coatings Technology 2005.
[94] Brady RF, Wake LV. Principles and formulations for organic coatings with tailored infrared properties. Progress in Organic coatings 1992;20:1–25.
[95] Thiele ES, French RH. Light-scattering properties of representative, morphological rutile titania particles studied using a finite-element method. Theory and Modeling of Glasses and Ceramics 1998;79:469–79.
[96] Gardner/Sward. Paint testing manual. 13th edition ASTM International; 1972.
[97] Licciulli A, Diso D, Torsello G, Tundo S. The challenge of high-performance selective emitters for thermophotovoltaic applications. Semiconductor Science and Technology 2003;18:174–83.
[98] Tomer V, Teye-Mensah R, Tokash JC. Selective emitters for thermophotovoltaics: erbia-modified electrospun titania nanofibers. Solar Energy Materials and Solar Cells 2005;85:477–88.
[99] Oelhafen P, Schüler A. Nanostructured materials for solar energy conversion. Solar Energy 2005;79:110–21.
[100] Niu F, Cantor B, Dobson PJ. Microstructure and optical properties of Si–Ag nancomposites films prepared by co-sputtering. Thin Solid Films 1998;320:184–91.
[101] Wang Q, Yang B, Tian D, Xiong G, Zhou Z. The optical properties of Ag–Si nanocomposite films prepared by sputtering. Surface and Coatings Technology 2000;131:404–7.
[102] Sheng P. Theory for the dielectric function of granular composite media. Phys Rev Lett 1980;45:60.